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ISOTHERMAL SINTERING OF METALLIC
POWDERS UNDER PRESSURE

- USSR -

[Following is a translation of an article by M. Yu. Bal'shin and A. A. Trofimova in the Russian language periodical Izvestiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk, Metallurgiya i Toplivo (News of the Academy of Sciences, USSR, Department of Technical Sciences, Metallurgy and Fuel), No 6, Moscow, Nov/Dec 1961, pages 45-51.]

This report deals with sintering under pressure of powdered copper, nickel and iron of varying finenesses. The sintering was done in a special dilatometer with graphite press-forms, at several temperatures and under pressures from two to 64 kg/sq cm. Pressure was applied on reaching a required level of temperature, heating rate being about 12 deg/min. Duration of isothermal treatment was 256 minutes, with recordings of change in sample size being made at intervals of 1, 2, 4, 8, 16, 32, 64, 128 and 256 minutes. Sintering and cooling took place in a hydrogen atmosphere.

During sintering under pressure, a powder conglomerate contracts both from relative displacement or slipping of the particles (interparticle deformation) and from irreversible deformation of the particles themselves (intraparticle deformation) (a). Tests have shown that both these types of deformation take place within the first few minutes of sintering.

Experiments are especially conclusive when sintering copper powders, obtained from solidification of fused copper cable having particles of true spherical form. Under contraction from interparticle shifting alone, contact between particles of these powders can occur only at discrete points; formation of large flat contact areas can then occur only because of irreversible deformation in the individual particles.

For example, coarse powdered copper of spherical particle form (0.04-0.063 mm) was heated at a pressure of 32 kg/sq cm to 950° in approximately one minute. Microphotographs of samples (Fig. 1) show in a substantial number of particles the flat contact areas that are formed by intraparticle deformation. At the same time many contacts are seen to be of a point-contact nature, which verifies the simultaneous occurrence of interparticle shifting.

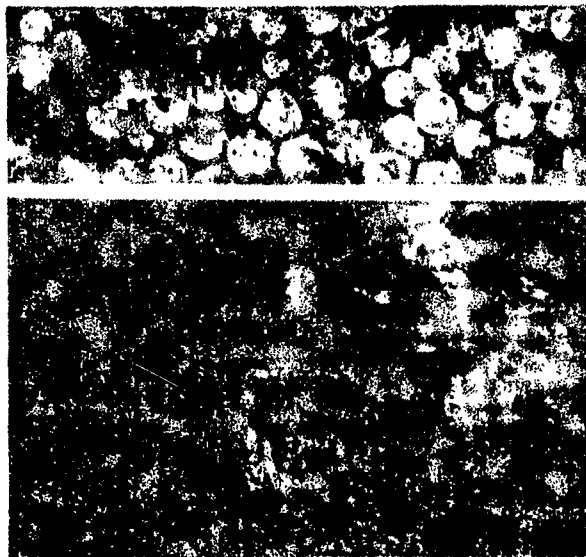


Figure 1. Microphotographs of granulated copper, sintered at 950° under 32 kg/sq cm for one minute. a-200X, b-500X

It must be emphasized that upon sintering, the porosity does not decrease to the maximum density value for spherical particles (25%), but only to 33%. In principle such a degree of contraction could be achieved due to interparticle deformation alone; however in this case irreversible intraparticle deformation also did occur.

Irreversible intraparticle deformation in the vicinity of the contact area may occur from plastic deformation or from flow (creep) of the particle mass -- or from a combination of both these processes. Pilot tests in studying the kinetics of change in an individual contact during heating under constant pressure (b) have shown that it is deformed due to both plastic deformation and creep. In this case the plastic deformation was essentially already completed within the first minute of the test, with creep deformation then taking place during later intervals.

It was noted in (b) that in the initial stages of sintering plastic deformation is unavoidable, since where contact area approaches zero, contact pressure approaches infinity, and in any case exceeds the critical pressure level S_k at which plastic deformation begins; thus in any event, contact areas during the first minute of heat and pressure application are formed as a result of irreversible plastic deformation of the contacting particles. During the second to the fourth minutes, with contact area loading now less than S_k , irreversible deformation continues due to creep. Many other researchers suggest that during sintering

not only continuous flow of material but also plastic deformation takes place (c,d).

As Table 1 shows, a large percentage of the total volumetric change in the granular mass occurs in the first minute of sintering, during the time of plastic deformation; the percentage rises with increased pressure.

Table 1
Sintering of electrolytic copper
at 900°: ratio of volume change in
first minute to total change in
256 minutes, as a function of
pressure.

Pressure, kg/sq cm	$\frac{(\Delta v)_1}{(\Delta v)_{256}}, \%$
8	25
16	46
32	54
64	68

One means of determining instantaneous rate of volume contraction, dv/dt , in the initial moment, was by graphical differentiation, using the tangent to the v-t curves at the appropriate point and taking v as the relative volume. In this case,

$$\frac{dv}{dt} = \frac{\tan \theta}{v'/t'} \quad (1)$$

where θ is the angle between the tangential line and the abscissa, v'/t' is the scale factor for v and t as chosen for the graph, and dv/dt is the rate of contraction of the relative volume of the granulated mass. (Note—the quantity dv/dt is proportional to the instantaneous rate of contraction $dv/v_0 dt$, where v_0 is initial relative volume of the granular mass but is constant for a given material, not depending on pressure or temperature).

The rate dv/dt decreases in approximately inverse proportion to time. As an example, let the scale factor v'/t' be such that for $(dv/dt)_1$ at the end of the first minute, $\tan \theta = 1$. Also let

$$(dv/dt)_{50} = \frac{(dv/dt)_1}{50} \text{ at the 50th min.}$$

$$(dv/dt)_{100} = \frac{(dv/dt)_1}{100} \text{ at the 100th min.}$$

$$(dv/dt)_{200} = \frac{(dv/dt)_1}{200} \text{ at the 200th min.}$$

Then the tangent values are respectively 0.02, 0.01 and 0.005; for the chosen scale the graphically found values of $\tan \theta$ at 50, 100 and 200 minutes practically coincide, even though the rates (dv/dt) are seen to be in a 4:2:1 ratio. If the scale factor v'/t' in the last portions of the $v - t$ curve be increased by 100 times relative to the initial portions, then $\tan \theta$ becomes

2, 1 and 0.5 respectively for the 50, 100 and 200 minute times and dv/dt can be found graphically with sufficient accuracy.

The graphical error in determining $\tan \theta$ (or $\cot \theta$) is $\pm 0.02-0.03$, with adequately objective drawing of the tangent. For $\tan \theta = 1$, error is also 2-3%; for $\tan \theta = 0.5$ or 2, 4-6%, and for $\tan \theta = 0.2$ or 5 the error is as high as 10-15%. Thus the graphical method is accurate enough only when using a scale factor for which $\tan \theta$ lies between 0.05 and 2. Even in this case, the method is very laborious and does not exclude the possibility of appreciable subjective error.

A less laborious method and one that is free of subjective error is the calculation of instantaneous rate dv/dt from the mean contraction rate $\Delta v/\Delta t$ in the time interval $t=t_2-t_1$. According to Lagrange's Theorem,

$$\Delta v/\Delta t = (dv/dt)_x \quad (2)$$

where $(dv/dt)_x$ is the instantaneous rate at the moment t_x , taken in the interval t_2-t_1 .

In ordinary sintering (e) and also, as our results showed, in sintering under pressure, the kinetics of contraction in a fine powder are adequately expressed by the equations

$$dv/dt = 1/mt \quad (3)$$

$$\Delta v = \frac{\ln(t_2-t_1)}{m} \quad (3a)$$

[where m is a constant. (Note- the minus sign has been omitted from dv and Δv .) After substituting values of dv/dt and m from equations (3) and (3a) into (2) we get

$$(dv/dt)_x = 1/mt_x = \frac{\Delta v}{\ln(t_2/t_1)_x t_x} = \Delta v/\Delta t$$

$$t_x = \frac{\Delta t}{\ln(t_2/t_1)} \quad (4)$$

In the event, as in this case, that $t_2/t_1 = 2$, then

$$t_x = \frac{\Delta t}{\ln(t_2/t_1)} = 1.44t_1 \quad (5)$$

For a less rapid dropoff of contraction rate with time than in (3), which would be the case for coarse granules, for $t_2/t_1 = 2$ we have

$$1.44t_1 \leq t_x \leq 1.5t_1 \quad (6)$$

Analysis shows that in these cases for determination of $(dv/dt)_x$ using the $1.44t_1$ value in (4) and (5) yields a somewhat low value, with an error not worse than 4%. Conversely, our studies have shown that for faster dropoff of contraction rate than given by (3), calculations from (4) and (5) give a slightly high value, with error again less than 4%. Comparing results from both the graphical and analytical determination of instantaneous contraction rate, the latter is preferable, using equations (4) and (5).

According to Williams (c), the rate of volume contraction under pressure sintering takes on a constant value with time. This view is erroneous, based on the above described drop in accuracy in graphical determination of dv/dt when using identical scales for the initial and final portions of the curve; and it is not borne out by Williams' own data. According to our data, a continuous decrease in contraction rate dv/dt occurs with time -- see Fig. 2 and Table 2.

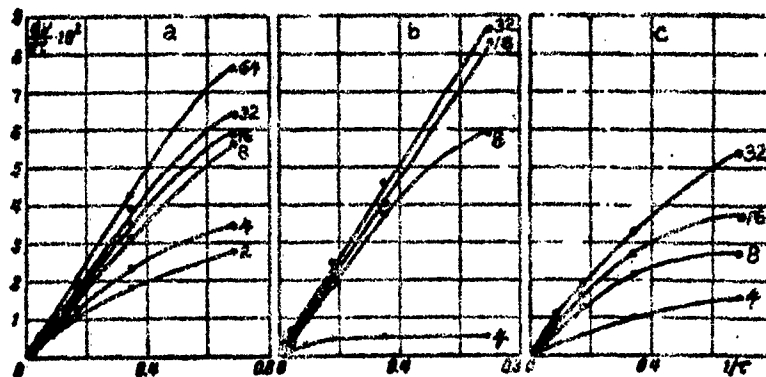


Figure 2. Dependence of powder contraction rate on sintering time, for various pressures. Curve numbers are pressures, kg/sq cm.

- a - electrolytically deposited Cu, temperature = 700°
- b - fine nickel carbonyl, 950°
- c - jet-powdered iron (under 90 microns), 860°

Table 2

Change in contraction rate dv/dt
with time in isothermal pressure
sintering of electrolytically
deposited copper, nickel carbonyl
and jet-powdered iron.

Material	Granule, microns	$T_{sint}, ^\circ C$	P, kg/sq cm	$\frac{(dv/dt)_{1.44}}{(dv/dt)_{184.7}}$
Copper	to 5	700	2	40.0
			4	45.0
			8	80.0
			16	100.0
			32	180.0
			64	160.0
Nickel	to 5	950	4	12.00
			8	108.00
			16	115.00
			32	170.00
Iron	to 90	860	32	99.52
			16	60.00
			8	37.52
			4	34.28
	to 90	960	32	29.50
			16	22.95
			8	21.88
			4	13.55
	150-250	860	32	75.50
			16	49.32
			8	42.20
			4	24.80

Iron	150-250	960	32 16 8 4	30.55 33.60 16.60 20.80
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In Fig. 3 is shown the variation in relative density ϕ of the powdered materials with time of isothermal sintering treatment. These graphs show the impossibility of drawing a straight line through any three points of a curve; thus intervals with a linear relationship of ϕ to t are lacking -- that is, portions with constant contraction rate $d\phi/dt$. (Note-the impression that the curves of Fig. 3 attain a linear character after a long time is false, based on the previously cited decrease in accuracy in determining $\tan \theta$ when using the same scale for drawing all the portions of the curve).

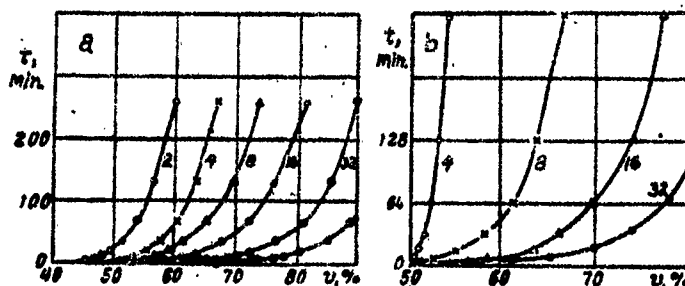


Figure 3. Powder density vs. sintering time at various pressures. Curve numbers are pressures, kg/sq cm.
a-electr. deposited Cu, 700°
b-fine nickel carbonyl, 950°

For fine powders, especially under sufficiently heavy pressures, contraction varies in almost inverse proportion to the interval of isothermal treatment, in accordance with equation (3), and the decrease in rate of contraction is practically independent of pressure for a given interval t . For coarse powders contraction rate also falls off continuously with time, although more slowly than the fine type, and contraction rate does increase with pressure.

From the data of Fig. 3 we may calculate the relationship of contraction rate to pressure during sintering. For example, the contraction of electrolytically fine copper (Fig. 3a) from $\phi = 61\%$ to 66.2% at 4 kg/sq cm pressure took 174 minutes, but at 8 kg/sq cm it needed only 44 minutes to reach the same volumetric contraction. Letting $V =$ contraction rate, the ratio of contraction rates is

$$V_2/V_1 = (\Delta t)_1/(\Delta t)_2 = 3.98$$

whereas the pressure ratio $p_2/p_1 = 2$, thus

$$V_2/V_1 = (p_2/p_1)^n \quad (7)$$

from which, after substituting corresponding values of V_2 , V_1 , p_2 and p_1 we obtain $n = 2$ for the given example. With change in sintering pressure on copper powder from two to 64 kg/sq cm , the value of n remained effectively constant. Values of n for the different powders are given in Table 3, which shows n varying from 2 to 5. If we exclude the case of sintering iron at a heat

slightly above that of the α to β transformation, then n varies from 2 to 3.9.

Table 3

Sintered Material	$T_{\text{sint}}, ^\circ\text{C}$	n
Iron (to 90 micron)	860	2.0-2.4
" "	960	4.0-5.0
" (150-250 micr.)	860	2.0-3.0
" "	960	3.5-4.5
Nickel carbonyl	950	2.9-3.7
Electrolytically deposited Cu	700	2.0-2.1

From reference (c), $n = 2$ to 3.2; from the data of (a), under conditions of effective sintering at quasi-viscous flow, $n = 2$. Values of n greater than 2 can be mostly explained as due to a more appreciable grain size, and by loss of activation in the powder at lower pressures, where a longer time is needed to attain a given degree of contraction.

The deviation of n from the value 2 can also be explained by other factors. Contraction of the powder, as noted earlier, occurs not only because of

deformation at individual contacts but also from the relative shifting of the particles. Under increased pressures the ratio of these two effects alters in favor of the more rapid one, i.e. particle shifting, due to which fact the quantity n can be larger than 2.

The contraction rate of copper and nickel powders is inversely proportional to treatment time only at sufficiently high pressures (see Fig. 2, Table 2). At pressures below 8 kg/sq cm for copper or 16 kg/sq cm for nickel, the powder is actually sintered under a pressure $(p+p_K)$, where p = applied pressure and p_K is capillary pressure; the latter may only be neglected when applied pressure greatly exceeds it. With increase in contact surface and sintering time the value of p_K , and hence of $(p+p_K)$, increases. Thus in the case of copper and nickel (Fig. 2, Table 2) when p is less than 8 and 16 kg/sq cm respectively, the quantity $(p+p_K)$ increases with sintering time, with the result that at low pressures there is a slower dropoff in contraction rate than at high pressures.

The slower decrease in contraction rate for coarse powders of low activity (Fig. 2, Table 2) is explained by the slower drop in activity of these

when compared to the fine powders at a given time. Regarding the high values of the exponent n in equation (7), the contraction rate can be markedly increased in sintering grain-filled masses such as porous filters, under pressure. Thus if $n = 3$ or 4 and $p_k = 1 \text{ kg/sq cm}$, as for coarse powders, then at an applied p of 10 kg/sq cm the sintering speed goes up 10^n times, that is, by a factor of 10^3 or 10^4 . Such increases in sintering speed are readily achievable in practice.

Conclusions:

1. Plastic deformation plays an active part in the first two or three minutes of pressure sintering.
2. Pressure increases sintering speed after the initial minutes by the relation

$$V_1/V_2 = (p_1/p_2)^n \quad \text{where } n \gg 2.$$

3. The decrease in sintering speed of powders, especially coarse types, is offset by a reducing of pressure. For dispersed powders under high enough

pressures, the decrease in sintering speed for a given interval is practically independent of pressure.

4. Pressure effectively increases speed of sintering by increasing both plastic deformation and rate of creep.

BIBLIOGRAPHY

- a. M. Yu. Bal'shin, "Powdered Metal Science", Metallurgizdat (State Publishing House on Metallurgy), 1948.
- b. M. Yu. Bal'shin, "Summary of Studies on Heat-Stable Alloys", Izdatyel'stvo Akademii Nauk SSSR (Publication of the Academy of Sciences, USSR), Vol 2, 1958, pages 359-369.
- c. J. Williams, Conference on Powder Metallurgy, London, 1956, pages 112-124.
- d. G. V. Samsonov, M. C. Koval'chenko, "Some Governing Relations in Sintering Powders of Refractory Compounds in a Heat Press", Izvestiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk, Metallurgiya i Toplivo (News of the Academy of Sciences, USSR, Department of Technical Sciences, Metallurgy and Fuel), No 4, 1959, pages 143-147.
- e. M. Yu. Bal'shin, Zhurnal Tekhnicheskoi Fiziki (Journal of Technical Physics), 1952, page 1230.

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